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The preparation and Research on the Electromagnetic Shielding Effectiveness of T-ZnO@Ag/Silicone Rubber Composites

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This study first conducted surface modification of Ag-plated Tetrapod-like zinc oxide (T-ZnO) whiskers with the use of dopamine and prepared Ag-plated T-ZnO whiskers (T-ZnO@Ag) by means of chemical plating, in which $AgNO_3$ solutions with different concentrations were used during the preparation. Micro-structures of the prepared T-ZnO@Ag powders were examined to evaluate the effect of $AgNO_3$ concentration on Ag plating performance. Subsequently, conductive Si rubber samples were prepared, the T-ZnO@Ag powders were used as fillers, and the effectiveness of the related electromagnetic shielding was investigated in detail. The results showed that using $AgNO_3$ solution with a concentration of 20 g/L, a continuous Ag coating-layer was observed on the surface of T-ZnO whiskers. It was evident that, when used as fillers, T-ZnO@Ag has a conductive threshold and when the mass fraction of the fillers exceeded 50 %, the T-ZnO@Ag whiskers that were uniformly dispersed in the matrix formed interconnected conductive paths. In this condition, the electromagnetic shielding effectiveness of the prepared T-ZnO@Ag/Si rubber composite reached up 90 dB.
Keywords: electroless plating, Ag-plated T-ZnO whiskers, conductive Si rubber, electromagnetic shielding; composite material.

1. INTRODUCTION

Electromagnetic shielding silicon (Si) rubber is currently one of the most favored electromagnetic sealing materials. After processing, it is a kind of functional rubber material and has extensive application in many industries, including aviation and space, ships, computers and power electronics, in which the Si rubber and the conductive fillers are used as the matrix and the shielding agent, respectively [1]. High-conductivity or high-magnetic-conductivity metal powders such as silver (Ag) powder, copper (Cu) powder and nickel (Ni) powder or metallic composite powders such as Ag-coated Ni powders, Ag-coated Cu powders and Ag-coated aluminum (Al) powders have been used as conductive fillers in conventional electromagnetic shielding Si rubber [2, 3]. However, these powder materials have several disadvantages, such as excessive cost, high density, and great filler consumption. There is an urgent need to overcome these issues in the development of electromagnetic shielding technology. Ag-plated or Ni-plated composite particles that are prepared via chemical deposition, using light-weight and low-cost glass beads, zinc oxide (ZnO), silicon dioxide (SiO_2) and glass fiber, appear to be attractive conductive fillers that can overcome limitations of conventional fillers [4 – 10].

Tetrapod-shaped zinc oxide (T-ZnO) is a kind of crystal whisker with regular three-dimensional structures [11 – 13]. Because of the advantages, such as light weight, high temperature resistance, and stable chemical properties, T-ZnO now is widely applied as a kind of rubber filler. Despite its poor electromagnetic absorption, the conductivity of T-ZnO can be improved by means of electroless plating; because of its special 3D space structure, conductive channels are easily formed in Si rubber, thereby giving it excellent electromagnetic shielding effectiveness (SE) [14].

In recent years, silver plating after modification by dopamine gradually has become a mature preparation route [15, 16]. Dopamine is a nonhazardous and environmentally-friendly material. This study first used dopamine for surface modification of T-ZnO whiskers, then reduced Ag^+ by glucose, and finally successfully plated a layer of Ag on the surface of T-ZnO. After being modified, the dopamine layer on the surface of the T-ZnO can be combined with Ag^+ to form a kind of chelate. Additionally, this study investigated the effect of the concentration of silver nitrate ($AgNO_3$) solution on the morphology and conductive performance of the Ag-plated T-ZnO and also examined the effect of the mass fraction of T-ZnO/Ag on the conductive and electromagnetic shielding performance of the prepared composite materials.

2. EXPERIMENTAL PROCEDURE

2.1. Material and preparation

Pure T-ZnO whiskers (99 wt.%) provided by Chengdu Crystrealm Co., Ltd was used as a raw material. The T-ZnO

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whiskers were placed in deionized water, subjected to suction filtration and elution, and dried for standby application. Firstly, the surface of the T-ZnO whiskers was modified. 2 g/L dopamine hydrochloride and 0.5 g/L tri-hydroxymethyl aminomethane sulfate (THAMS) was added to a 10 g/L T-ZnO suspension and the mixture was stirred for 24 hours. After suction filtration and drying, the modified T-ZnO whiskers with surface-deposited dopamine were prepared. Next, $AgNO_3$ solutions with different concentrations were prepared and $NH_3 \cdot H_2O$ was added gradually to the prepared $AgNO_3$ solutions for the preparation of silver ammonia solution (also referred to as Tollens' reagent). 0.5 g/L povidone (PVP) was then added to the silver ammonia solution for stabilization and dispersion. Subsequently, 10 g/L of the dopamine-modified T-ZnO whiskers was added to the mixture, which was stirred for 30 minutes so that the suspension of the dopamine-modified T-ZnO whiskers was prepared. During the stirring process, a lot of Ag^+ ions are adsorbed around the modified T-ZnO whiskers due to chelation between the Ag^+ and the polydopamine. Finally, glucose was added to the mixture as a reducing agent and the Ag-plated layer was deposited on the surface of the T-ZnO whiskers. After room-temperature stirring for 1.5 hours, suction filtration and drying, the Ag-plated T-ZnO whiskers (T-ZnO@Ag) were prepared.

The inhibitor, Si rubber (3450B), cross-linking agent and T-ZnO whiskers before and after Ag plating were added to Si rubber (3450 A) in an appropriate order and the mixture was stirred thoroughly. After uniform mixing, the mixtures underwent vacuum defoaming in a vacuum oven and then were poured into cylindrical molds with a diameter of 150 mm and a thickness of 2 mm. The prepared samples were pressurized and vulcanized on a pressure vulcanizer, during which the vulcanizing temperature and pressure were set as 160 °C and 15 MPa, respectively. Finally, two different kinds of composite material, T-ZnO/Si rubber and T-ZnO@Ag/Si rubber, were prepared.

2.2. XRD and morphology observation

Phase analysis was conducted using an automatic X-ray diffractometer (XRD) (D/Max2200PC, Rigaku, Japan). Scanning electron microscopy (SEM) (ZEISS EVO18, ZEISS Ltd., Germany) was used to observe the distribution of the fillers in the composites and their tensile fracture morphology.

2.3. Measurements of SE

The SE of samples under plane-wave conditions was measured by means of the flange coaxial method. The setup consisted of a DN15115 SE tester, which was connected to an Agilent 4396B RF network spectrum impedance analyzer. The scanning frequency ranged from 100 MHz to 1.5 GHz. The thickness of the rubber layers was 2 mm.

3. RESULTS AND DISCUSSION

The XRD patterns of T-ZnO whiskers before and after Ag plating are shown in Fig. 1. It can be observed that XRD spectrum of T-ZnO fits perfectly with the standard XRD spectrum of ZnO with hexagonal Wurtzite structure. Additionally, the XRD spectrum of T-ZnO exhibits narrow and sharp diffraction peaks and no other unknown peaks, suggesting that the prepared T-ZnO was characterized by high crystallinity and excellent purity. After chemical silvering, the diffraction peaks of face-centered cubic Ag (1 1 1), (2 0 0), (2 2 0) and (3 1 1) were located at $2\theta = 38.2°$, 44.4°, 64.6° and 76.7°, respectively. The observations confirmed that the T-ZnO whiskers were coated by Ag on the outside surface, which can affect both the adsorption and scattering of the T-ZnO spectrum. Moreover, the T-ZnO@Ag particles were larger, thereby weakening the diffraction peaks of the T-ZnO.

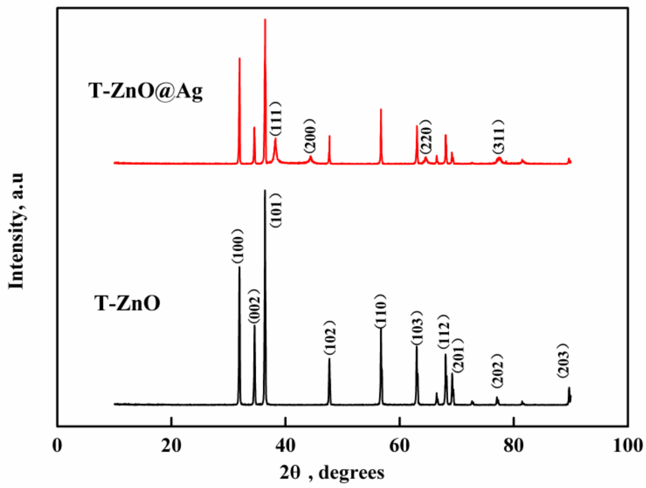

Fig. 1. XRD patterns of the prepared T-ZnO and T-ZnO @Ag whiskers

The morphologies of the prepared T-ZnO, T-ZnO@Ag whiskers and Si-rubber-based composite materials are shown in the SEM micrographs presented in Fig. 2. As shown in Fig. 2 a, the T-ZnO whiskers had a smooth surface appearance, the lengths of the tetrapod-like whiskers ranged from 10 to 30 μm, the base diameter was approximately 0.8 ~ 1.5 μm, and the angle between any two whiskers was nearly 109°. Fig. 2 b shows the SEM image of T-ZnO@Ag that was prepared using 10 g/L $AgNO_3$ solution, from which it can be observed that the formation of the Ag layer on the surface of T-ZnO whiskers was discontinuous and incomplete and there was an increase in the diameter of the T-ZnO whiskers. Fig. 2 c shows the SEM image of T-ZnO@Ag that was prepared using the 20 g/L $AgNO_3$ solution. The T-ZnO whiskers were coated with a complete and compact Ag layer obviously. Fig. 2 d shows an SEM image of T-ZnO@Ag that was prepared using the 30 g/L $AgNO_3$ solution, from which it can be observed that the Ag layer on the surface of T-ZnO whiskers was thicker and more compact than was the case in Fig. 2 b and Fig. 2 c. Fig. 2 e – h) display SEM images of the composite materials of Si rubber and T-ZnO@Ag whiskers that were prepared using different concentrations. It can be observed that the T-ZnO@Ag whiskers were uniformly staked in the Si rubber matrix and formed an interconnected conductive network.

Volume resistivity also is an important parameter for shielding materials. The T-ZnO@Ag power was made into a cylindrical piece with a size of about Φ10×1mm, and the resistivity was tested by four-probe method. Three samples were tested for each concentration, and three points were measured for each sample.

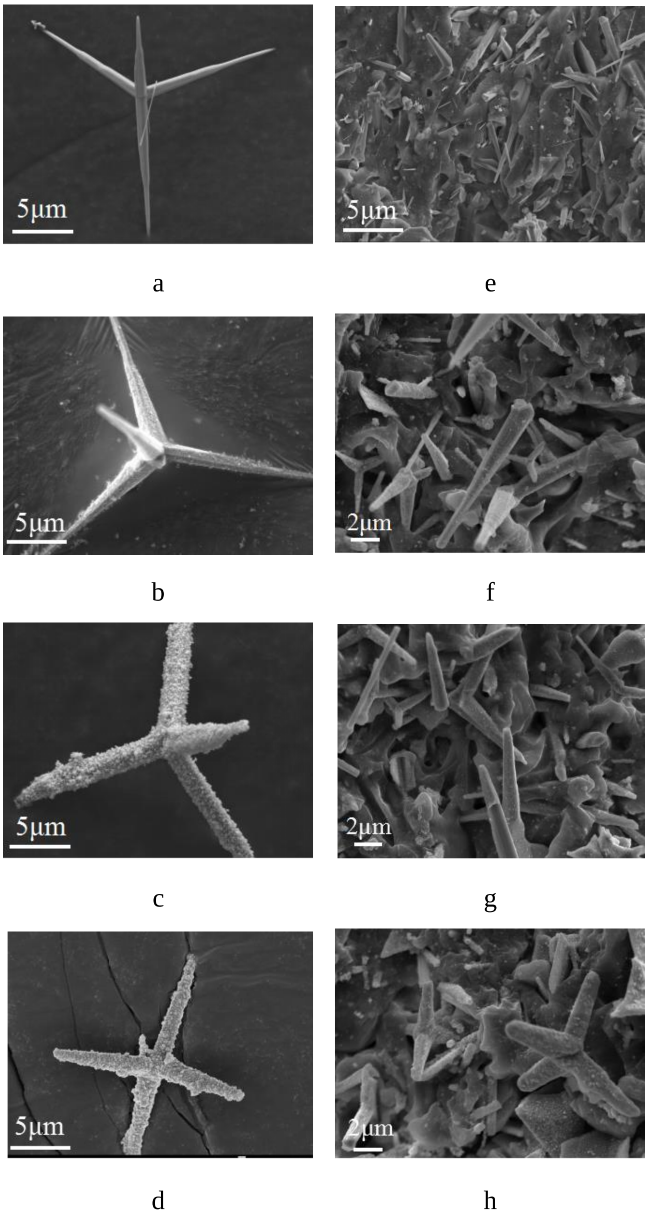

Fig. 2. SEM images of T-ZnO (a) and T-ZnO@Ag whiskers that were prepared using different concentrations of $AgNO_3$: b – 10 g/L; c – 20 g/L; d – 30 g/L; SEM images of different Si-rubber-based composite materials: e – T-ZnO/Si rubber; f, h – T-ZnO@Ag/Si rubber (10 g/L, 20 g/L, 30 g/L $AgNO_3$).

Table 1. Volume resistivities of T-ZnO@Ag powder and T-ZnO@Ag/Si rubber composite materials when different concentrations of $AgNO_3$ solutions were used

Sample No.	Concentration of $AgNO_3$ solution, g/L	Volume resistivity of T-ZnO@Ag, Ω·cm	Volume resistivity of T-ZnO@Ag/Si rubber, Ω·cm
1	10	1.69×10^{-2}	3.43×10^{-1}
2	20	2.51×10^{-4}	1.04×10^{-3}
3	30	2.34×10^{-4}	1.03×10^{-3}

The composite resistivity test method is similar to powder, and the sample size is Φ 150 × 2 mm. All resistivity test data are on the same order of magnitude.The final data list in the tabal 1 is the intermediate value. Table 1 lists the volume resistivities of the T-ZnO@Ag powder and the T-ZnO@Ag/Si rubber composite materials when different concentrations of $AgNO_3$ were used. The volume resistivity of the T-ZnO@Ag powder that was prepared using 10 g/L $AgNO_3$ was 1.69×10^{-2} Ω·cm. As the concentration of $AgNO_3$ was increased to 20 g/L, the volume resistivity of the T-ZnO@Ag powder decreased to 2.51×10^{-4} Ω·cm. With further increase in the concentration of the $AgNO_3$ solution, the volume resistivity of the T-ZnO@Ag powder remained almost unchanged. This was due to the fact that, using 20 g/L $AgNO_3$ solution, a continuous and compact Ag layer was formed on the surface of the T-ZnO. The measurement results for volume resistivity are in good agreement with the SEM observations. The optimal concentration of $AgNO_3$ in the preparation of the whiskers was determined to be 20 g/L.

According to percolation theory, fillers that originally were isolated and scattered can form continuous conductive paths when the volume fraction of the filler reaches a critical value. At the macro level, the volume resistivity of the composite system decreased suddenly, accompanied by an abrupt increase in the electromagnetic shielding performance. Fig. 3 shows the variation in the conductivity of the composites with different mass fractions of fillers. When the mass fraction of the filler was 50 %, the conductivity of the composite reached 1000 S/cm. The conductivity of the composite increased abruptly at a mass fraction of 40 % – 50 % of filler, suggesting that the percolation threshold of the T-ZnO@Ag particles was 40 % – 50 % and the corresponding mass fraction of the filler was 80 – 100 phr. Compared with glass beads and carbonyl-modified Ni powders, significantly fewer T-ZnO@Ag particles were used in this kind of composite material [17, 18].

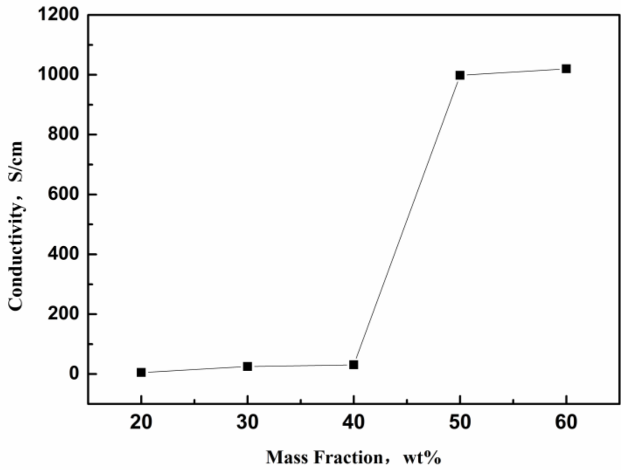

Fig. 3. Relationship between the mass fraction of filler and the conductivity of the composite

In combination with the above analysis of the percolation threshold, the mass fraction of T-ZnO@Ag particles in this study was determined to be 50 %. Next, the electromagnetic shielding effectiveness of the three different kinds of T-ZnO@Ag/Si rubber composites that were prepared using different concentrations of $AgNO_3$ solution were examined, and the test results are displayed in Fig. 4. When the concentration of $AgNO_3$ was 10 g/L, the electromagnetic shielding effectiveness is only about 30 dB because the Ag particles on the T-ZnO whiskers surface were not covered completely, as the concentration of $AgNO_3$ was increased to 20 g/L, the electromagnetic shielding effectiveness suddenly increased to 90 dB. It was due to a three-dimensional mesh structure with a certain size formed in the T-ZnO/silicone rubber composite materials. The innumerable ring-shaped conductive flow networks made of T-ZnO whiskers could disspate electromagnetic wave energy when the electromagnetic wave entered into the composite material, in addition, T-ZnO has a large aspect ratio，the sharp needle tip was likely to form a local strong electric field under the influence of the external electric field. In this case, all the needle tip of T-ZnO whiskers as an electric dipole resonated with the coming electromagnetic to reduce electromagnetic wave energy [12].

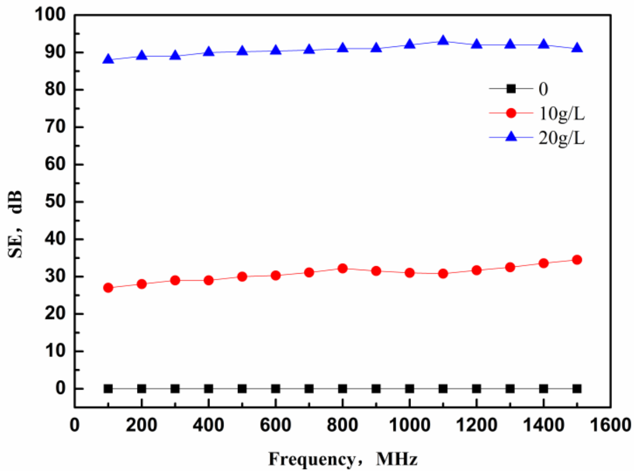

Fig. 4. The effectiveness of electromagnetic shielding by the conductive si rubber filled with the silver-coated T-ZnO powders with different silver nitrate contents: 0, 10 g/L and 20 g/L

According to the electromagnetic shielding theory proposed by Schelkunoff, the shielding effectiveness (SE) of a material can be written as:

$$SE = R + A + B, \quad (1)$$

where R, A and denotes the losses caused by reflection, absorption and multiple reflections, with a unit of dB.

In case of $A > 10$ dB, B is negligible and Eq. 1 can be simplified as:

$$SE = R + A, \quad (2)$$

Specifically,

$$R = 1\ 68 - 10\ \lg(f\mu/\sigma). \quad (3)$$

and

$$A = 1.31t\sqrt{f\mu\sigma}, \quad (4)$$

where μ and σ denote the relative permeability and conductivity of the shielding material, respectively; f denotes the electromagnetic frequency, with a unit of Hz; t denotes the thickness of the shielding material, with a unit of mm.

It can be concluded that the decline in volume resistivity can increase both reflection loss (R) and adsorption loss (A), thereby enhancing shielding effectiveness. In conclusion, with increasing concentration of the $AgNO_3$ solution, the electromagnetic shielding effectiveness of the T-ZnO@Ag/Si rubber composite was increased.

4. CONCLUSIONS

This study first prepared Ag-plated T-ZnO whiskers through dopamine modification and chemical Ag plating, in which different concentrations of $AgNO_3$ solutions were used, and then prepared different conductive Si rubber samples in which both T-ZnO and T-ZnO@Ag were used as the conductive fillers, respectively. Moreover, the micro-morphologies of the T-ZnO@Ag whiskers and the electromagnetic shielding effectiveness of the prepared conductive Si rubber composites were examined in depth.

T-ZnO exhibited a representative hexagonal Wurtzite structure with a regular and smooth surface. Using $AgNO_3$ solution with a concentration of 20 g/L, the surface of T-ZnO whiskers can be coated with a continuous and complete Ag layer.

After being added to Si rubber, the T-ZnO@Ag powder can be dispersed uniformly in the matrix, whose conductive threshold was 50 wt.%. In terms of filler consumption and conductivity, the prepared conductive Si rubber, in which T-ZnO@Ag powder was used as the filler exceeded the electromagnetic shielding performance of composites with other fillers. The new composites offer the prospect of wide application.

When the mass fraction of T-ZnO@Ag was 50 %, the conductivity of the Si-rubber-based composite reached 1000 S/cm, and the shielding effectiveness at an electromagnetic frequency range of 100 – 1500 MHz was up to 90 dB, suggesting that the T-ZnO@Ag powder formed interconnected conductive paths in the matrix. Thus, T-ZnO@Ag/Si rubber composites have a bright future in electromagnetic shielding service.

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